THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 4 – 2010, ISSN 1453 – 083X

MORPHOLOGICAL ASPECTS OF THERMOSETTING POLYMERS/Zn COMPOSITE COATINGS

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ABSTRACT

The present work has the purpose of studying the morphological aspects of composite coatings having zinc matrix and thermosetting polymers (PF resin type NOVOLAC - RESITAL 6358/1 and epoxy resin type DINOX 110L) as dispersed phase obtained during the electrodeposition process of zinc. The composite coatings layers were electrodeposited from a suspension of resin particles in aqueous zinc sulphate electrolyte by adding 10g/L resin particles with size 0.1 - 5μm into electrolyte solution. The structure of the coatings was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) methods. The surface morphology of thermosetting polymers/Zn composite coatings layers is different compared with pure zinc coatings: the regular crystal structure characteristic of electroplated zinc coatings was disturbed. The decreases in the roughness of composite coatings layers compared to roughness of pure zinc layers can be determined by the fine structure of the composite coatings.

KEYWORDS: electrodeposition**,** thermosetting polymers/Zn composite coatings, scanning electron microscopy, atomic force microscopy, roughness

1. Introduction

Early humans realized that for some uses, combinations of materials often produced properties in the mixed material, or composite, that were superior to those of the component materials themselves. A more useful but narrower definition of a composite intended for structural applications (i.e., a ‘‘structural composite’’) is that it is a combination of a structural reinforcing material in a binder or matrix material.

The key to this definition is that the component materials act together, in concert, to help one another, often synergistically. An enveloping matrix provides protection from damage to reinforcements and adds structural stability to the reinforcements under compressive loading. At the same time, the reinforcing material or reinforcement enhances the strength, hardness, stiffness, and/or toughness of the matrix material.

Modern synthetic composites include every imaginable combination of metals, intermetallics, ceramics, glasses, polymers, and carbonaceous materials (e.g., graphite). A simple pictorialization of possible combinations is shown in Fig. 1 under the form of a Venn diagram.

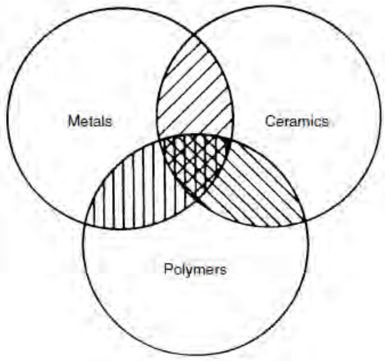


Fig. 1. *Venn diagram showing where composites fit among the fundamental materials of metals, ceramics (and glasses) and polymers.*

The intersection between any two, as well as among all three, fundamental materials represents a possible composite in which any material could be the matrix that surrounds the reinforcement, which could be any material. While the matrix material or phase is used to designate the category of composite, the reinforcement-surrounding matrix tends to give the composite its highest level properties (e.g. metallic qualities, ceramic qualities, polymeric qualities). This makes the reinforcing material or reinforcement extremely important, as it usually imparts the functionally specific properties (e.g., strength, hardness, stiffness, toughness, sensing, actuation, etc.) [1 – 4].

Direct structural information on the surface changes due to dissolution and deposition can be obtained by sensitive techniques, such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). Each of these techniques resolves surface structure down to the nanometer scale. However, the image formation mechanisms are quite different, resulting in different types of information about the surface structure.

Since its invention in 1986 [5] atomic force microscopy AFM has become the most widely used form of scanning probe microscope (SPM) with applications in surface, materials and biological sciences [6 – 7]. AFM can create three-dimensional topographic images of surfaces in nanometer resolution and is capable to probe forces in the nanonewton range [8 – 9].

The present work has the purpose of studying the morphological aspects of thermosetting polymers/Zn composite coatings having zinc matrix and two types of thermosetting polymers: first - PF resin type Novolac with commercial name RESITAL 6358/1 synthesized by Hüttenes – Albertus Group (Germany) and the second - epoxy resin type DINOX 110L synthesized by S.C. AZUR S.A. Timişoara (Romania) as dispersed phases obtained during electrodeposition process of zinc.

2. Experimental research

For electrodeposition it was used a zinc plating bath [10]. The pure zinc and composite coatings were obtained at current density of 4 A/dm^2, time for electrodeposition 30 minutes, a stirring rate of 1000 rpm, electrolyte temperature of 25^{0}C and pH of 3.8 – 4.4.

The PF resin/Zn composite coatings were electrodeposited from a suspension of phenol – formaldehyde (PF) resin particles in aqueous zinc sulphate electrolyte by adding 10g/L PF resin dispersed particles. The size of dispersed particles was of 0.1 – 5 µm.

Phenol-Formaldehyde resin is a highly cross linked thermosetting material that is produced by the poly-condensation of phenol and formaldehyde in the presence of either acidic or basic catalyst. An acid catalyst is usually used in preparing Novolac type resin. A Novolac resin is produced if the mole ratio of formaldehyde to phenol (F/P) is greater than one [11]. This method produces relatively linear chains with molecular weights typically between 500g/mol and 1000g/mol (see Fig. 2).

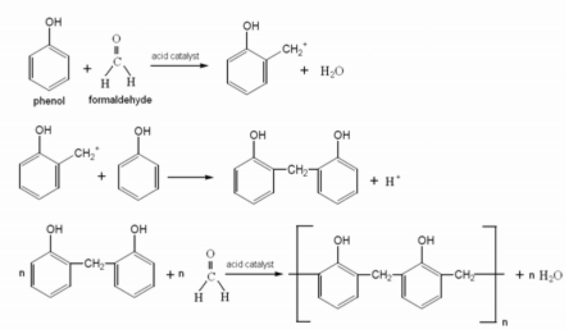


Fig. 2. *The schematic formation of the Novolac type structures.*

The properties of PF resin type Novolac (RESITAL 6358/1) used for obtaining composite coatings are presented in Table 1.

Table 1. *The properties of PF resin (RESITAL 6358/1)*

Property	Value
Molecular weight, g/mol	3392 – 3816
Melting point (DIN 53181)	70 – 80º C
Sliminess at 120^{0}C (DIN 53081/1)	35 – 45 Pa.s
Free phenol (DIN 16916/2)	< 1% (usually 0.7 – 0.8%)
Water (DIN 51777/1)	< 0.5 %
Flow length at 125^{0}C melting with 10% hmt (DIN 16916/2)	35 – 44mm
The product is not esterificated	

The epoxy resin/Zn composite coatings were electrodeposited from a suspension of epoxy resin particles in aqueous zinc sulphate electrolyte by adding 10g/L epoxy resin dispersed particles. The size of dispersed particles was of 0.1 – 5 µm.

The epoxy resins (also widely known as epoxide resins and, occasionally, as ethoxyline resins) are characterized by the possession of more than one 1,2 - epoxy group per molecule. This group may lie within the body of the molecule but is usually terminal. The large family of epoxy resins represents some of the highest performance resins of those available at this time. Epoxies generally out-perform most other resin types in terms of mechanical properties and resistance to environmental degradation, which leads to their almost exclusive use in aircraft components [12].

The schematic formation of the epoxy resin from bisfenol A and epichlorohidryn is presented in Fig. 3 [13] and the properties of epoxy resin type DINOX 110L used for obtaining composite coatings are presented in Table 2.

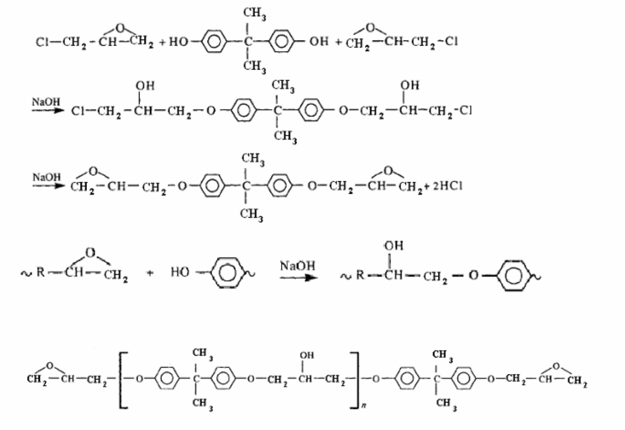


Fig. 3. *The schematic formation of the epoxy resin structures.*

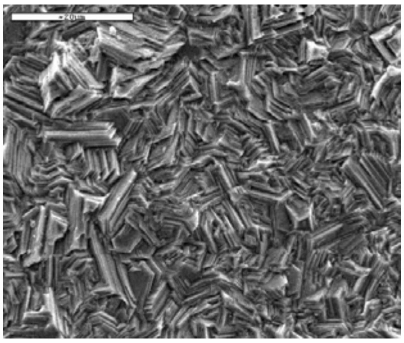
Table 2. *The properties of epoxy resin type DINOX 110L*

Property	Value
Molecular weight, g/mol	500
Density	1.18 – 1.25 g/cm^3
Epoxy parameter	0.185 – 0.220 equivalents in 100g resin 100%
Melting point	64 – 76ºC
Color of iodine	2 – 4 mgI$_2$/100cmc
Ash	Maximum 0.05%
Volatile substances contained	Maximum 1%

The morphologies of deposits were examined by Scanning Electron Microscope type JEOL, JSM-T220 A and Atomic Force Microscope type NanoWizard II.

3. Results and discussions

The morphological aspects of pure zinc coating and thermosetting resin/Zn composite coatings obtained by scanning electron microscopy method are compared in Figs. 4 – 6.



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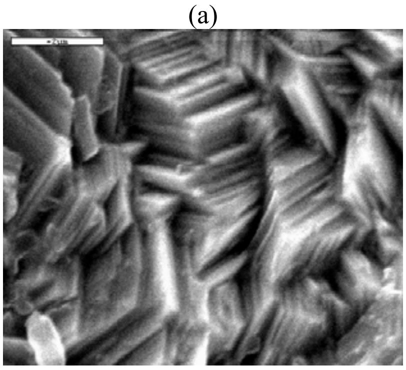
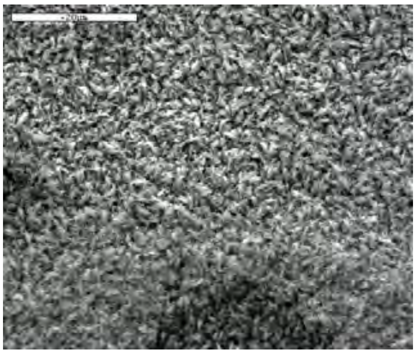


(b)

Fig.4. *SEM surface morphology of pure zinc coatings a - x 2000, b – x 15000*



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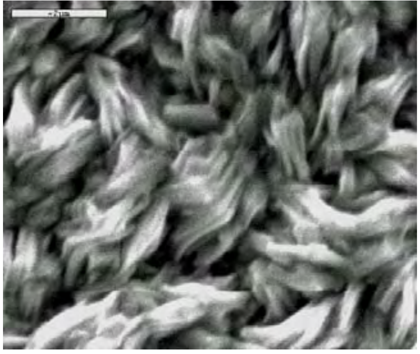
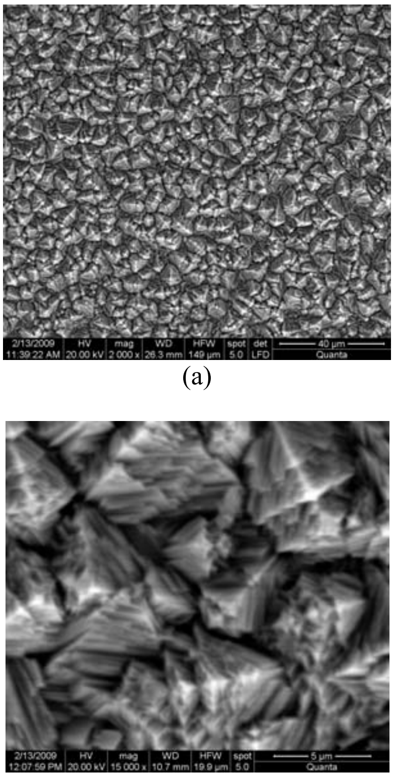


(b)

Fig.5. *SEM surface morphology of PF resin/Zn composite coatings a - x 2000, b – x 15000.*



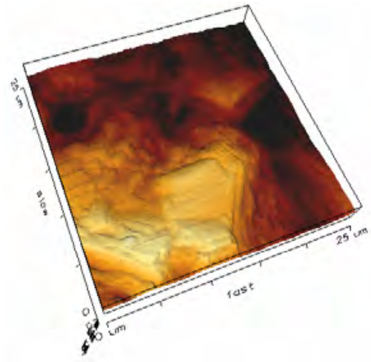
(a)

(b)

Fig.6. *SEM surface morphology of epoxy resin/Zn composite coatings a - x 2000, b – x 15000.*

It can be observed that the surface of zinc is made up of regular crystals. The resin particles codeposited with zinc radically change the structure of the metal: they disorder the regular crystal structure and the structure of the zinc matrix becomes finely crystalline. The pure zinc coatings have a rather regular surface, whereas the composite coating surfaces have finer grains structure with particles of resin uniformly distributed on the surfaces.

The surface structure of pure zinc coatings and thermosetting resin/Zn composite coatings under atomic force microscope are presented in Figs. 7 – 9.



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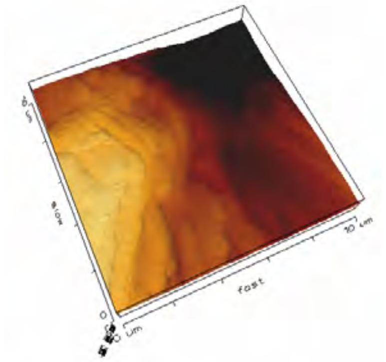
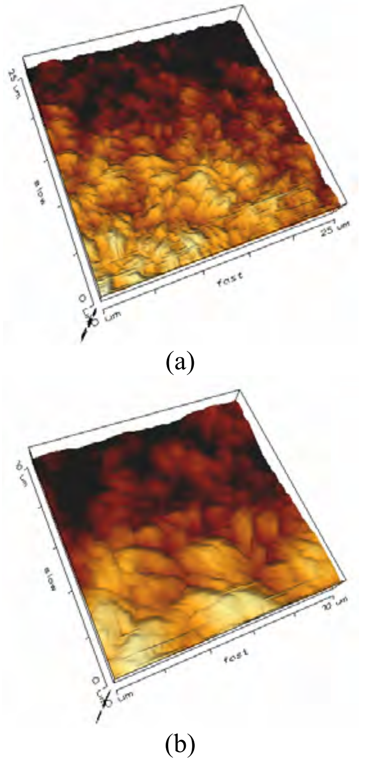


(b)

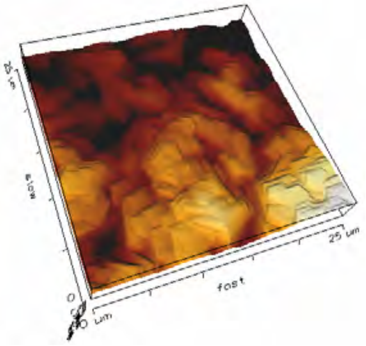
Fig.7. *AFM 3D images of surface morphology for pure zinc coatings a – 25µm x 25µm, b – 10µm x 10µm.*



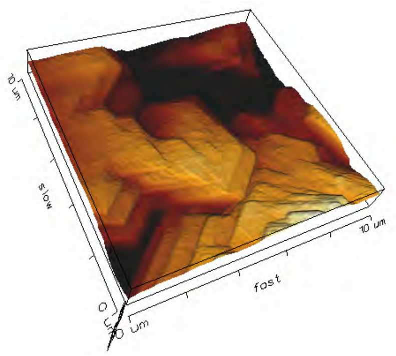
(a)

(b)

Fig.8. *AFM 3D images of surface morphology for PF resin/Zn composite coatings a – 25µm x 25µm, b – 10µm x 10µm*



(a)



(b)

Fig.9. *AFM 3D images of surface morphology for epoxy resin/Zn composite coatings a – 25 x 25µm, b – 10 x 10µm.*

From the AFM images, it can be said that the surface of zinc is made up of regular hexagonal crystals with a uniform grain size. The PF resin and epoxy resin particles codeposited with zinc radically change the structure of the metal: they disorder the regular crystal structure and the structure of the zinc matrix becomes finely crystalline.

The histograms of the scanned surfaces are presented in Fig.10.

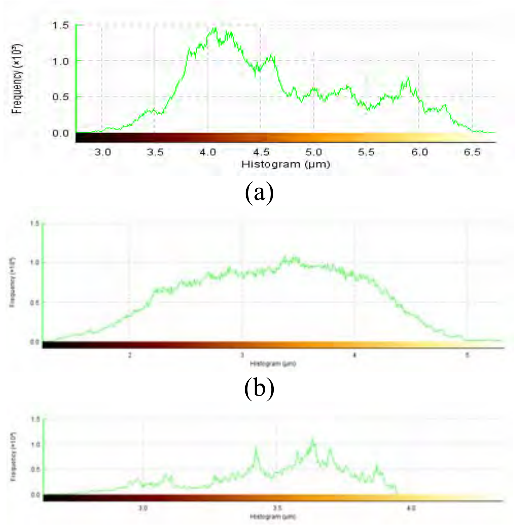


Fig. 10. *The histograms of the scanned surfaces 25µm x 25µm for pure zinc (a), PF resin/Zn (b) and epoxy resin/Zn (c)*

Roughness is a measure of the texture of a surface and plays an important role in determing how a real systtem will interact with the environment. It is quantifed by the vertical deviations of a real surface from its ideal form. If these deviations are large, the surface is rough; if they are small the surface is smooth.

The variation of roughness is presented in Fig. 11.

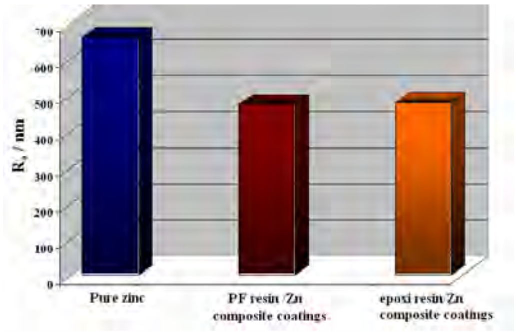


Fig. 11*. Variation of roughness for pure zinc coatings and thermosetting/Zn composite coatings.*

The thermosetting polymer type PF resin and epoxy resin acts as reducing the crystals size of electrodeposited zinc during co-deposition.

The thermosetting polymer could have an inhibition effect on zinc crystals growth and a catalytic effect in increasing nucleation sites.

4. Conclusions

It has been demonstrated that the thermosetting polymer type PF resin and epoxy resin particles could be codeposited with zinc to obtain composite coatings.

The surface morphology of PF resin/Zn and epoxy resin/Zn composite coatings layers is different compared with to pure zinc coatings: the regular crystal structure characteristic of electroplated zinc coatings was disturbed.

The resin particles embedded in the zinc matrix perturb the zinc crystals growth during electrodeposition.

From the analyses of histograms and variation of roughness it can be concluded that by adding the PF resin and epoxy resin particles in the zinc electrolyte solution the roughness of the composite coatings layers compared to the roughness of pure zinc layers decreases.

These decreases in the roughness of composite coatings determined changes the surface structure of composite coating to finer crystallites and smoothness.

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